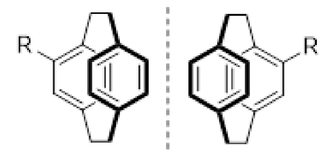
TETRATHIAFULVALENE-[2.2]PARACYCLOPHANES: SYNTHESIS, CRYSTAL STRUCTURES AND CHIROPTICAL PROPERTIES [1]

Cécile Mézière[1], Magali Allain[1], Cristina Oliveras-González[1], Thomas Cauchy[1], Nicolas Vanthuyne[2], Laura G. Sarbu[3], Lucian M. Birsa[3], Flavia Pop[1], Narcis Avarvari[1]

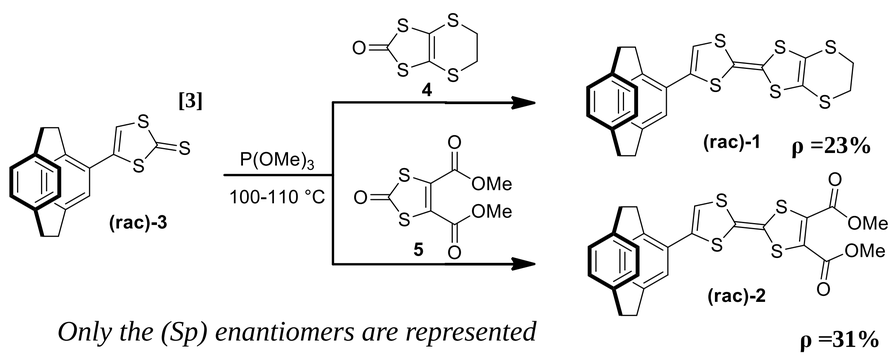
[1]Laboratoire MOLTECH-Anjou, UMR6200 CNRS-Université d'Angers, Faculté des Sciences, Bât. K, 2 Bd Lavoisier, 49045 Angers Cedex, France
[2]Aix Marseille Université, CNRS, Centrale Marseille, iSm2, Marseille, France
[3]Department of Chemistry, "Al. I. Cuza", University of Iasi, Iasi, Romania

Objective: **Planar chirality is introduced in electroactive tetrathiafulvalenes via paracyclophanes units in order to explore the chiroptical properties of the new compounds formed. The challenge is also to investigate the influence of chirality on conductivity properties of the corresponding mixed valence salts that could be obtained by electrocrystallization as previously described in our group [2].**



The two enantiomers of monosubstituted [2.2]paracyclophane: R_P S_P

Synthesis: heterocoupling in the presence of phosphite



Only the (Sp) enantiomers are represented

Purification of the coupling products is achieved by chromatography on silica gel ; The bis [2.2]paracyclophane TTF is not formed.

Enantiomer resolution by chiral HPLC:

On Chiralpak IE (250 x 10 mm), hexane/ethanol/dichlorométhane (5/3/2), 5 mL/min, UV detection at 254nm.

(rac)-1 ⇨ **(-)-enantiomer ee > 98.5% (*Sp*)**
(+)-enantiomer) ee > 99% (*Rp*)

(rac)-2 ⇨ **(-)-enantiomer ee > 99%**
(+)-enantiomer) ee > 99%

Cyclic voltammetry:

Two one electron reversible oxidation processes for (rac) *1* and *2*

Compound	E^1ox	E^2ox
1	**0.02**	0.47
2	**0.14**	0.62
TTF-$(SMe)_2$ [3]	0.03	0.35
Ph-TTF-$(SMe)_2$ [4]	0.00	0.37

No significant influence of the paracyclophane unit on the oxidation potentials.

The electron withdrawing effect of the carbonyl units in **2** reduces its donor ability.

Half wave potentials relative to Fc/Fc^+, DCM 10^{-1} M $TBAFP_6$, 20 ° C

Frontier molecular orbitals:

MO	Energy	1
LUMO	-1.42 eV	
HOMO	-4.94 eV	

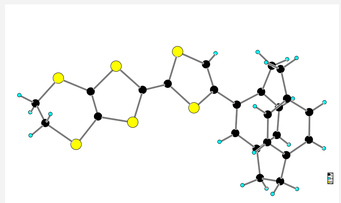
MO	Energy	2
LUMO	-1.97 eV	
HOMO	-5.11 eV	

The HOMO corresponds to the TTF moiety and the stability is higher for compound 2 ; In **1** the LUMO is based on the cyclophane unit while in **2** it is spread over the ester part.

Crystal structures:

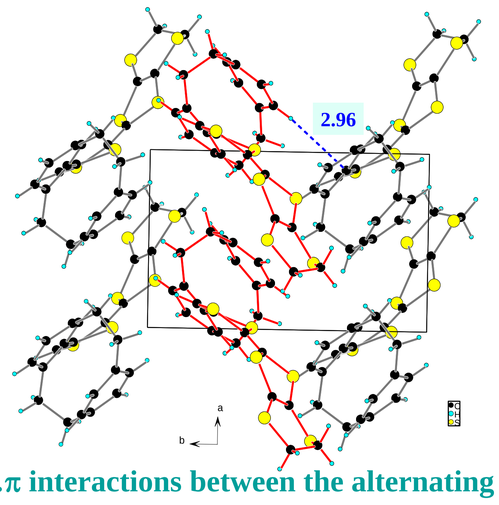
The crystals were obtained after slow evaporation of an acetonitrile solution in a very thin tube [4]

(*Rp*)-1



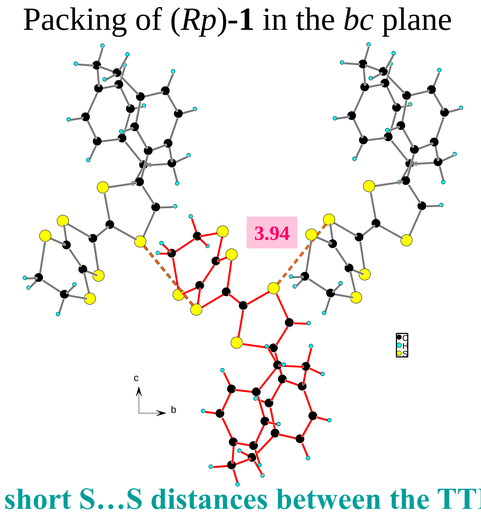
Crystal size: 0.216 x 0.148 x 0.038 mm
T = 200.0(1) K, λ = 1.54184 Å :
a = 7.4706(2)Å α = 90°
b = 11.7648(3)Å β = 100.454(3)°
c = 13.0617(4)Å γ = 90°
V = 1128.94(5) Å^3
R_1 = 4.80%
Monoclinic non centrosymetric space group, P 2_1

Packing of (*Rp*)-**1** in the *ab* plane



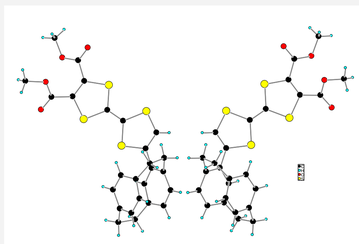
ArH…π interactions between the alternating stacks

Packing of (*Rp*)-**1** in the *bc* plane



Lateral short S…S distances between the TTF units of the orthogonal molecules

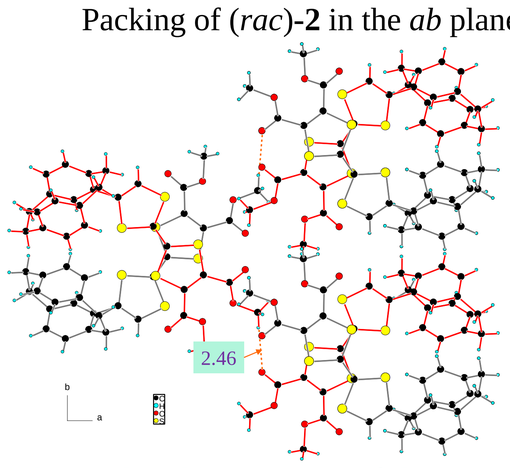
(*rac*)-2



Crystal size: 0.394 x 0.030 x 0.023 mm
T = 150.0(1) K, λ = 1.54184 Å
a = 17.0529(9) Å α = 90°
b = 12.6806(3) Å β = 113.142(6)°
c = 17.1325(9) Å γ = 90°
V = 3406.6(3) Å^3
R_1 = 8.31%
Monoclinic non centrosymetric space group, P 2_1

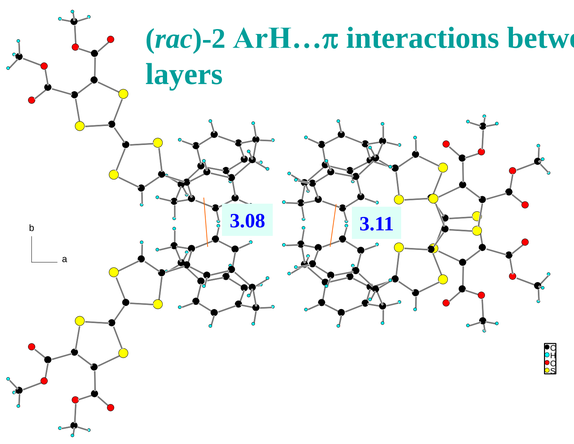
ArH…π interactions between the alternating stacks but no S…S one : high distorsion compared to (*Rp*)-1 (less favorable packing)

Packing of (*rac*)-**2** in the *ab* plane



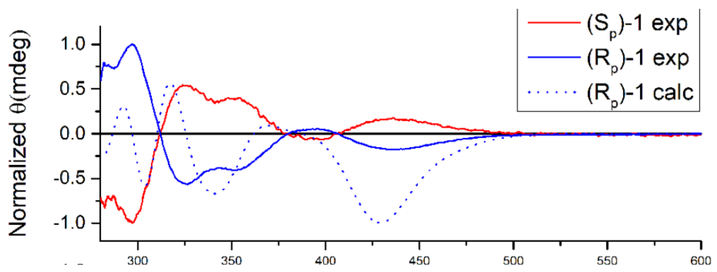
Hydrogen bond interactions of the ester units

(*rac*)-2 ArH…π interactions between layers

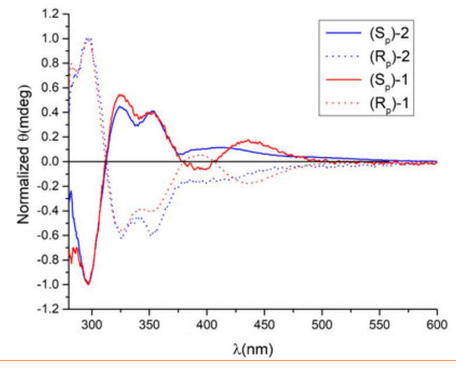


Segregation of the TTF and the p-cyclophanes units

Circular dichroïsm:



First intense band at 296 nm, two bands at 325 (S_0 to S_4 excitation) and 350 nm, followed by one large band of weak intensity for enantiomers of *2*, and two bands of low intensity at 395 (S_0 to S_3 excitation) and 435 nm (S_0 to S_2 excitation) for the enantiomers of compound ***1***. There is a small blue shift of all bands compare to the calculated data. The TD-DFT calculation method is not suitable for compound ***2*** because of gas phase position of ester groups, heavily distorded from the TTF median plan, generating an artificial CD signal.



[1] Mézière C., Allain M., Oliveras-González C., Cauchy T., Vanthuyne N., Sarbu L.G., Birsa L.M., Pop F., *Chirality*, 2018, 30, 568.
[2] Pop F., Auban-Senzier P., Canadell E., Rikken G.L.J.A., Avarvari N., *Nat. Commun.*, 2014, 5, 3757.
[3] Sarbu L.G., Bahrin L.G., Jones P.G., Birsa L.M., Hopf H., *Beilst. J. Org. Chem.*, 2015, 11, 1917.
[4] Spingler B., Schnidrig S., Todorova T., Wild F., *Cryst. Eng. Comm.*, 2012, 14, 751.
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